



Short communication

An electrochemically compatible and flame-retardant electrolyte additive for safe lithium ion batteries

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H I G H L I G H T S

- ▶ A phosphazenic compound as a flame-retarding electrolyte additive is synthesized.
- ▶ The self-extinguishing time value of 10% PNP in the electrolyte is 40% decreased.
- ▶ No significant impact on performance of electrode in 10% PNP electrolyte is observed.

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In this paper, we prepared a phosphazenic compound triethoxyphosphazene-N-phosphoryldiethylester (PNP) by a facile method and characterized as a flame-retarding electrolyte additive for lithium ion batteries. The flammability and electrochemical performance of the PNP-containing electrolyte were investigated. The self-extinguishing time (SET) value of 10% PNP in the electrolyte is 40% decreased compared to base electrolyte, implying strong inhibition to the flammability. The electrochemical performances of MCMB/Li, LiFePO₄/Li and LiMn₂O₄/Li half-cells in 10% PNP electrolyte exhibit considerable capacity, coulombic efficiency and cycling stability compared to the base electrolyte. Therefore, PNP as flame-retarding additive is a promising candidate combining efficient flame retardancy and good electrochemical performance for safer lithium ion batteries.

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1. Introduction

Lithium ion batteries are now actively developed as a clear power for electric vehicle (EV) and hybrid electric vehicle (HEV) to alleviate CO₂ emissions and environmental pollution [1]. A severe obstacle in the technology development is the safety concern of lithium ion batteries. Since the state-of-the-art electrolytes of lithium ion batteries use highly flammable carbonate-based organic electrolytes, which might be ignited and then possibly causes serious hazards of firing and explosion under abused conditions (heat, overcharge, short-circuit etc.) [2]. To solve this problem, many safety technologies have been suggested, including the use of fire-retardant electrolyte [3], redox shuttles [4,5], potential-sensitive separator [6] and temperature-sensitive electrode coating [7]. Among these approaches, the flame-retardant

electrolyte or nonflammable additive seems to be a simplest and most effective method for battery applications.

In previous works, a vast diversity of nonflammable solvents, such as fluorinated ether [8,9], organic phosphorus compounds and ionic liquids [10,11], have been tried as an additive or a co-solvent of the electrolytes. Among them, the organic phosphoric compounds including phosphates, cyclic phosphazenes and their derivatives seem to be a promising candidate of nonflammable electrolytes because of their high flame retardancy, low pollution and electrochemical stability in the normal operation region. Though most phosphates such as trimethyl phosphate (TMP), cresyl di-Ph phosphate (CDP), dimethyl methylphosphonate (DMMP) etc. [12–15], have relatively high flame-retardant efficiency, they always show strong reductive decomposition on the graphite anode, resulting in poor cycling performance. Fortunately, the poor anode compatibility of phosphate additives can be alleviated to some extent by the use of proper electrolyte additives to build stable solid electrolyte interface (SEI) film on the anode surface [16]. On the contrary, the cyclic phosphazenes show a better cell performance,

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but relatively lower efficiency for suppressing flammability compared to phosphates [3,17]. Recently, Xu et al. [18] used tris(2,2,2-trifluoroethyl) phosphate (TFP) as a cosolvent to gain a balance between the nonflammability and electrochemical performance of the electrolyte. However, due to potential toxicity and high cost of fluorinated solvent, it is better to develop low polluting, high efficient and low-cost nonflammable electrolyte using phosphorus-based fire-retardants.

Based on the previous researches, we designed a phosphazenic compound, $(\text{EtO})_2\text{P}(\text{O})-\text{N}=\text{P}(\text{OEt})_3$ (PNP), which combines the structure of the nonflammable phosphate and electrochemical stable phosphazene for achieving a compatibility between the nonflammability and electrochemical performance. In this paper, we report 10% PNP in electrolyte can give an obvious flame-retarding and excellent electrochemical performance.

2. Experimental

All the chemicals except for CCl_4 and acetonitrile were commercially available without further purification. CCl_4 and acetonitrile were dried by CaH_2 while the remained was used. Triethoxyphosphazene-N-phosphoryldiethylester (PNP) was synthesized according to the reference [19] by the one-pot reaction of triethyl phosphite, diethyl phosphite, sodium azide and CCl_4 in acetonitrile at 80°C (Scheme 1). The synthetic reaction proceeded with two steps, the intermediate $(\text{EtO})_2\text{P}(\text{O})-\text{N}_3$ was firstly produced by the reaction of diethyl phosphite, sodium azide and CCl_4 , then reacted with triethyl phosphite to release N_2 and the target compound. After no gas evolved, the mixture was filtered and the filtrate was distilled to remove the solvent and then distilled under vacuum to yield a colorless liquid ($132\text{--}134^\circ\text{C}$ (<3.5 torr), the value in reference [20] is 110°C (0.05 torr)), yield: 42% based on diethyl phosphite. ^1H NMR (300 MHz, CDCl_3): δ /ppm 4.1–4.3 (m, 6H, $-\text{N}=\text{P}(\text{OCH}_2\text{CH}_3)_3$), 4.0 (t, 4H, $(\text{CH}_3\text{CH}_2\text{O})_2\text{P}(\text{O})-$), 1.2–1.4 (m, 15H, all $-\text{CH}_3$); IR: 2981 cm^{-1} (m), 1325 cm^{-1} (m), 1228 cm^{-1} (m), 1033 cm^{-1} (s). The IR bands of 1325 cm^{-1} and 1228 cm^{-1} are characteristic vibration of $\text{P}=\text{N}$ group and $\text{P}=\text{O}$ group respectively, which is good agreement with the reference [21].

The 1 M LiPF₆ in DMC:EC:EMC (1:1:1, by volume) electrolyte was selected as a base electrolyte. The base electrolyte and its mixtures with different concentrations of PNP electrolyte were prepared in an argon-filled glove box (Mikrouna superstar). Self-extinguishing time (SET) normalized against electrolyte mass was used to evaluate the flammability of the electrolytes, which measured in the similar procedure as used by Xu et al. [3,18], a glass-fiber ball of 3–5 mm diameter was placed on an “O” shaped iron shelf (Fig. 1), the whole shelf was weighed and tarred, then the glass-fiber ball was soaked into the electrolyte for several seconds absorbing 0.1–0.2 g electrolyte, taken out onto “O” shaped iron shelf and weighed, after that, the whole shelf was moved to a bracket, followed by igniting the wet glass-fiber ball and recording the time took for the flame to extinguish. Each sample was repeated at least eight times. The conductivity of the selected

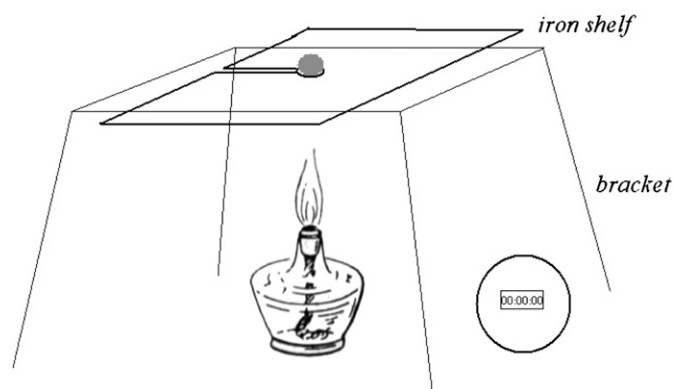


Fig. 1. Schematic diagram of SET test.

electrolyte was measured on DDS-307 (INESA Scientific Instrument Co., Ltd, Shanghai, China) in 25°C constant temperature water bath.

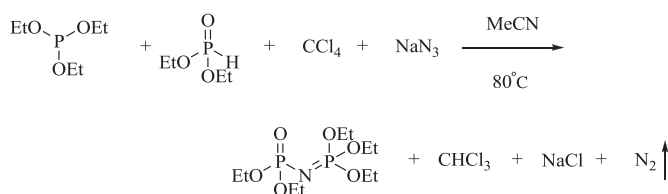
The electrochemical stability of electrolytes on anode and cathode materials were measured by Cyclic Voltammetry (CV). CV experiments were performed on CHI600C Electrochemical Analytical Instrument (Chenhua, Shanghai, China) in three-electrode electrochemical cell with a Pt disk of 0.5 mm diameter as working electrode, Li foil as both reference electrode and counter electrode.

Cell performance was achieved on a multi-channel battery cycler (Land CT2001A, Wuhan, China) by assembling CR2016 coin cells of MCMB/Li, $\text{LiFePO}_4/\text{Li}$ and $\text{LiMn}_2\text{O}_4/\text{Li}$ in the glove box. These cells were cycled between a setted range of voltage (MCMB/Li : 0–3 V, $\text{LiFePO}_4/\text{Li}$: 3–4 V, $\text{LiMn}_2\text{O}_4/\text{Li}$: 3–4.3 V) using the current density of 40 mA g^{-1} . The negative electrode consisting of meso-carbon microbeads (MCMB) (90 wt.%), acetylene black (2 wt.%) and poly(vinylidene flouride) (PVDF) (8 wt.%) were used, while two kinds of positive electrodes were consisting of LiFePO_4 (80 wt.%), acetylene black (12 wt.%) and PVDF (8 wt.%); LiMn_2O_4 (85 wt.%), acetylene black (8 wt.%) and PVDF (7 wt.%), respectively.

3. Results and discussion

3.1. Flammability

In this study, self-extinguishing time (SET) was used to evaluate the flammability of the electrolytes. Fig. 2 shows the results of SET tests containing different concentrations of PNP in normal electrolyte. Because the SET value strongly depends on the absorbing amount and materials of electrolyte, the shape of the supporting materials and manual error by timing and airflow, each sample was tested for at least eight times and calculated their average value. As can be seen in Fig. 2, the SET value of DMC/EC/EMC-based electrolyte is 106 s g^{-1} while only 39 s g^{-1} for the electrolyte containing 20% PNP (by volume ratio) and 64 s g^{-1} for the electrolyte containing 10% PNP. A substantial reduction of 40% (42 s g^{-1}) with addition of 10% PNP for SET value is relatively higher than the flame retardants such as phosphates TMP, TEP (triethyl phosphate) and similar to cyclic phosphazene HMTP (hexamethoxycyclo-triphosphazene) [3], but less than TFP [18] and DMMP [22] which are nearly nonflammable at the addition of 10% and 20%, respectively. However, TMP, TEP and DMMP containing 10% in electrolytes all have a serious impact on anodic electrochemical performance [3,16]. PNP used here, 10% of the amount in electrolyte, not only exhibits obvious decrease on the flammability, but also doesn't have too much adverse influence on electrochemical property of the batteries as discussed below. The reason why PNP can play as a flame retardant may be contributed by the formation of free



Scheme 1. Synthesis of PNP.

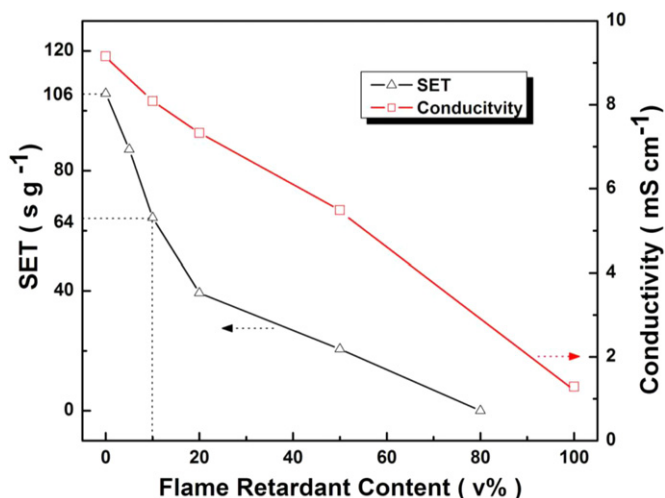


Fig. 2. The results of SET tests (black) and conductivity (red dots) of the electrolytes containing different concentration of PNP. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

radical [P] which could capture [H] and [OH] radicals produced by combustion of carbonate electrolyte [23]. Additionally, the conductivity of electrolyte with the different content of PNP was also carried out as shown in Fig. 2. The electrolyte conductivity drops almost linearly with increasing amount of flame retardant due to possible high viscosity and low dielectric constant of PNP. The ionic conductivity of electrolyte containing 10% PNP can reach ca. 8 mS cm^{-1} while ca. 7.2 mS cm^{-1} for 20% PNP, indicating an insignificant effect on electrolyte conductivity if adding PNP within certain limits.

3.2. Electrochemical properties of PNP-based electrolyte

Fig. 3 shows the CV curves of the electrolyte containing 10% PNP in the 1 M LiPF_6 DMC/EC/EMC (1:1:1) in a wide potential range from -0.2 to 5.0 V (vs. Li^+/Li). Besides a pair of reversible redox peaks due to lithium deposition and stripping in a potential range

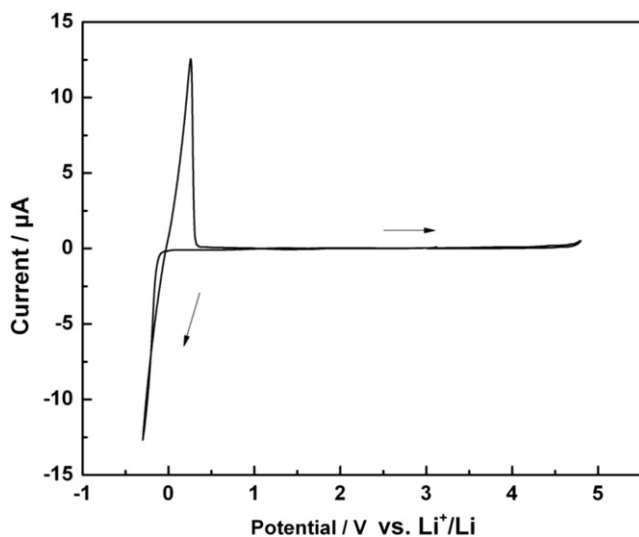


Fig. 3. Cyclic Voltammogram of the flame retardant PNP with an amount of 10% in the 1 M LiPF_6 DMC/EC/EMC (1:1:1) electrolyte using powder microelectrode, scan rate: 50 mV s^{-1} .

of -0.3 and 0.3 V , there were no apparent decomposition reactions of the PNP flame retardant observed within a wide electrochemical window, suggesting that PNP flame retardant is quite stable in operational potential range of lithium-ion batteries. Also, the electrochemical compatibility of PNP flame retardant electrolyte on anode materials (MCMB) and cathode materials (LiFePO_4 , LiMn_2O_4) were investigated as shown in Fig. 4. As it can be seen that in Fig. 4a there is a weak reduction peak in a potential range of 1 and 2.3 V during first negative scan, which may be attributed for the decomposition of solvent and disappears at second cycle for the formation of SEI film in the electrolyte containing 10% PNP on MCMB. The CV profile for 10% PNP-contained electrolyte on MCMB is very similar to that for the base electrolyte shown in inset of Fig. 4a, indicating that the electrolyte containing 10% PNP is well compatible with MCMB. For LiFePO_4 and LiMn_2O_4 cathode materials, the CV curves of both samples (Fig. 4b) have quite symmetrical redox peaks, similar to those of the previous reports [24–26]. This means that there is no effect on lithium insertion and extraction for

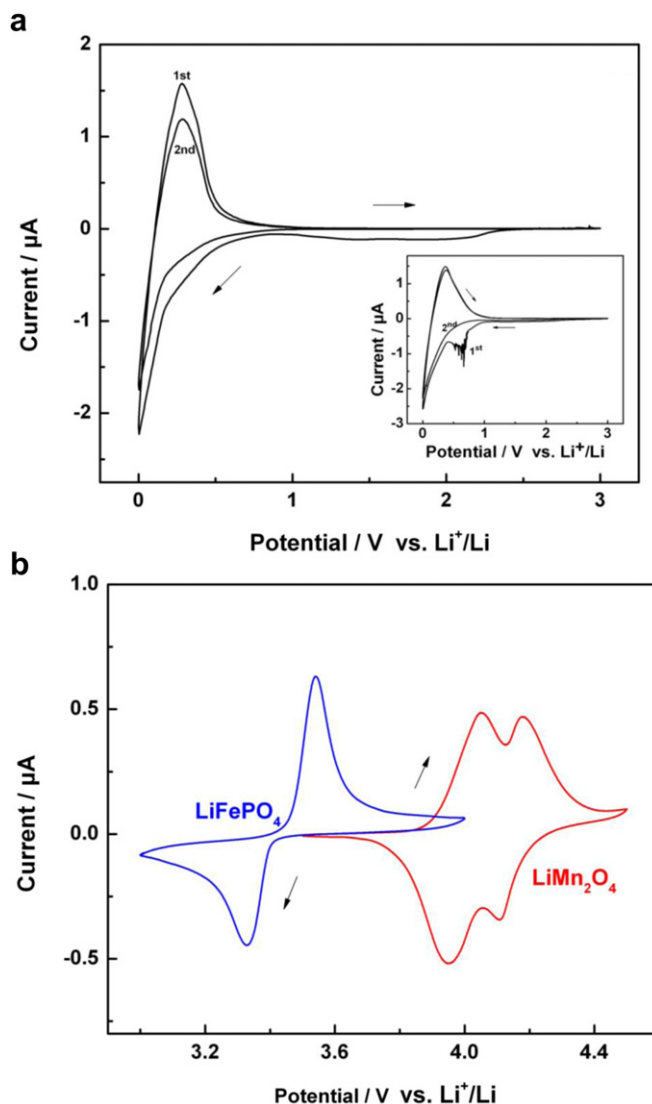


Fig. 4. CV performance of the flame retardant electrolyte (10% PNP in the 1 M LiPF_6 DMC/EC/EMC(1:1:1)) using powder microelectrode. (a) MCMB electrode, scan rate: 10 mV s^{-1} ; inset: CV of baseline electrolyte on MCMB. (b) LiFePO_4 (blue line) and LiMn_2O_4 (red line), scan rate: 1 mV s^{-1} . (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

LiFePO₄ and LiMn₂O₄ cathode materials when adding 10% PNP in electrolyte. The CV results indicate that the electrolyte containing 10% PNP has an excellent compatibility and electrochemical stability on both anode and cathode materials and can serve as an efficient flame retardant for the application of lithium ion batteries.

3.3. Electrochemical characteristics in cells

To evaluate the effect of PNP on the cell performance, the electrochemical performance of MCMB/Li half-cells containing various concentrations of PNP was examined by galvanostatic cycling. Fig. 5a shows the charge/discharge curves of MCMB electrode in 10% PNP electrolyte at different cycle. Apparently, an irreversible discharge capacity due to the decomposition of electrolyte, emerges in slope potential range of 1.5–0.5 V in first cycle and disappears in successive cycles, which is in good agreement with the observation of CV result. The MCMB electrode displays an initial discharge/charge (insertion/extraction) specific capacity of 423 and 329 mAh g⁻¹ respectively, corresponding to the initial coulombic efficiency of 77%, which is very close to that without PNP

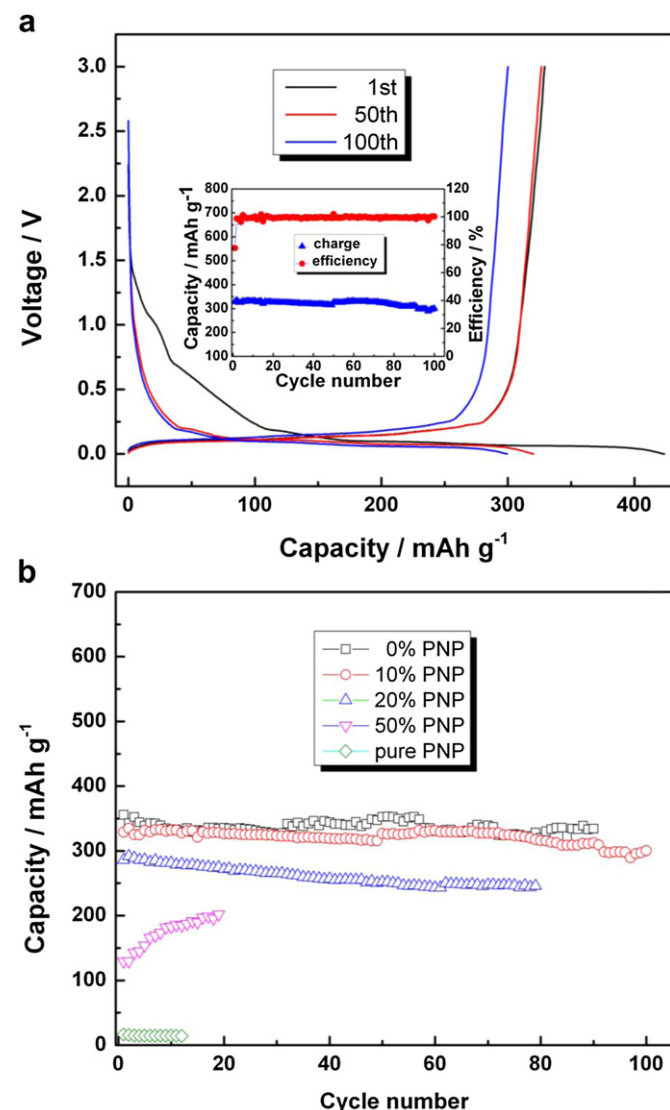


Fig. 5. a) The electrochemical performance of MCMB/Li half-cell with electrolyte of 10% PNP-containing; b) the charge specific capacity of MCMB/Li half-cells against cycle number with the electrolytes containing various concentrations of PNP, for electrolytes containing 50% PNP and pure PNP each has less than 20 data points.

electrolyte (80.6%). The initial reversible capacity of MCMB electrode in the 10% PNP electrolyte is slightly lower compared to that observed from the base electrolyte (355 mAh g⁻¹) as shown in Fig. 5a, probably due to high viscosity, low ionic conductivity and wetting ability of PNP. The reversible capacity of MCMB electrode at 50th cycle and 100th cycle can still reach 326 and 300 mAh g⁻¹, corresponding to the capacity retention of 99% and 91%, respectively. Moreover, after the initial cycle, the coulombic efficiency of the electrode achieved to 98.8% at the second cycle and keep about 100% in successive cycles. These results imply that the electrolyte with 10% PNP has insignificantly impact on the capacity, coulombic efficiency and cycling stability of MCMB electrode. However, the impact on reversible capacity of MCMB electrode gradually outstands with increasing the amount of PNP in electrolyte. As can be seen in Fig. 5b, the MCMB electrode can deliver the reversible capacity of 286 mAh g⁻¹ in 20% PNP electrolyte while only 129 and 16 mAh g⁻¹ in 50% PNP and pure PNP electrolyte. This phenomenon also can be usually observed when adding other flame retardants [3], resulting from high viscosity, low ionic conductivity and wetting quality. In addition, when adding 50% PNP, it is obvious that the capacity of MCMB electrode gradually increases with cycling,

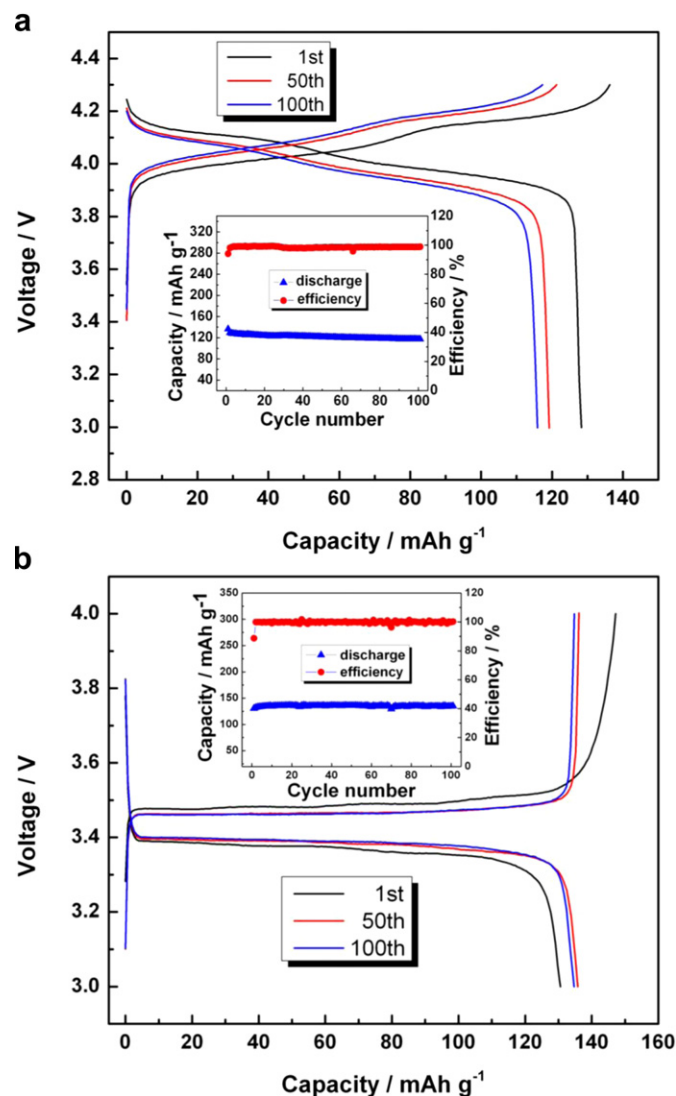


Fig. 6. The electrochemical performance of LiMn₂O₄/Li (a) and LiFePO₄/Li (b) half-cells with electrolyte of 10% PNP-containing.

suggesting that the electrolyte slowly penetrates into the interior of electrode with cycling. Therefore, for PNP, wetting compatibility is also an important factor on the electrochemical property of electrode. According to the above results, the electrolyte with 10% PNP can be chosen as flame-retardant electrolyte in terms of the balance between the nonflammability and electrochemical performance.

Fig. 6 shows the charge/discharge and cycling performance of LiMn_2O_4 and LiFePO_4 cathode materials in 10% PNP electrolyte. It can be seen in Fig. 6a that the charge/discharge curves of LiMn_2O_4 electrode exhibit two potential plateaus, in accord with the results of CV curve in Fig. 4b. The LiMn_2O_4 electrode delivers an initial reversible capacity of 128 mAh g^{-1} with a coulombic efficiency of 94%. After 100 cycles, the electrode still keeps 90% of its initial capacity, showing an excellent cycling stability of the LiMn_2O_4 electrode in 10% PNP electrolyte. For LiFePO_4 cathode (Fig. 6b), the results show the discharge capacity of 130 mAh g^{-1} in the initial cycle and improves up to 135 mAh g^{-1} after 100 cycles, showing no any discernible capacity decay. Based on these results, it could be concluded that the flame retardant 10% PNP electrolyte is well compatible with either MCMB anode or LiMn_2O_4 and LiFePO_4 cathode. The excellent electrochemical compatibility and flame retardancy of the 10% PNP electrolyte may arise from the reasons: (1) PNP has a mono phosphazene structure, which has a similar good electrochemical compatibility to phosphazene [3]. (2) PNP has strong flame retardancy due to a high phosphor content (19.5%). Therefore, PNP combines both a phosphazene structure with good electrochemical performance and phosphate structure with efficient flame retardancy, which is suitable to the application of flame-retardant lithium ion battery.

4. Conclusions

A bis-phosphazenic compound, PNP, is synthesized and characterized as a novel flame-retarding additive for lithium ion battery. It was found that the electrolyte containing 10% PNP obviously suppressed the flammability without serious sacrifice in cell performance. The electrochemical experiments of MCMB anode or LiMn_2O_4 and LiFePO_4 cathode in 10% PNP electrolyte show no significant effect on capacity, coulombic efficiency and cycling stability compared to the baseline electrolyte. Therefore, PNP apparently is a good choice of flame-retardant electrolyte for application of lithium ion battery.

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